Int J Life Cycle Assess (2014) 19:1745–1754
DOI 10.1007/s11367-014-0779-1



# Development of a dynamic LCA approach for the freshwater ecotoxicity impact of metals and application to a case study regarding zinc fertilization

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Received: 12 November 2013 / Accepted: 30 June 2014 / Published online: 17 July 2014


**Abstract**
*Purpose* Temporal variability is a major source of uncertainty in current life cycle assessment (LCA) practice. In this paper, the recently developed dynamic LCA approach is adapted to assess freshwater ecotoxicity impacts of metals. The objective is to provide relevant information regarding the distribution and magnitude of metal impacts over time and to show whether the dynamic approach significantly influences the conclusions of an LCA. An LCA of zinc fertilization in agriculture was therefore carried out.
*Methods* Dynamic LCA is based on the temporal disaggregation of the inventory, which is then assessed using time-horizon-dependent characterization factors. The USEtox multimedia fate model is used to develop time-horizon-dependent characterization factors for the freshwater ecotoxicity impact of 18 metals. Mass balance equations are solved dynamically to obtain fate factors as a function of time, providing both instantaneous (impact at time $t$ following a pulse emission) and cumulative (total time-integrated impact following a pulse emission) characterization factors (CFs).
*Results and discussion* Time-horizon-dependent CFs for freshwater ecotoxicity depend on the emission compartment and the metal itself. The two variables clearly influence metal fate aspects such as the maximum mass loading reaching freshwater and the persistence time of metals into this compartment. The time needed to reach the total impact for each metal may exceed thousands of years, so the time horizon used in the analysis constitutes a determining factor. The case study reveals that the results of a classical LCA are always higher than those obtained from a dynamic LCA, especially for short time horizons. For instance, at the end of a 100-year fertilization treatment, only 25 % of the impacts obtained through traditional LCA occurred.
*Conclusions* Results show that dynamic LCA enables assessing freshwater ecotoxicity impacts of metals over time, allowing decision makers to test the sensitivity of their results to the choice of a time horizon. For the particular case study of zinc fertilization over a period of 20 years, the use of time-horizon-dependent CFs is more important in determining the dynamics of impacts than the timing of emission.

**Keywords** Dynamic LCA · Fate · Freshwater ecotoxicity · Metals · Multimedia model · Time horizon

## 1 Introduction

Life cycle assessment (LCA) is a recognized tool to assess the potential environmental impacts of products or services, and researchers are investing efforts to reduce the uncertainty of the outcomes. Temporal variability is a major source of uncertainty associated with the inventory and impact characterization phases (ISO 2006).

Inventory accounts for all the emissions from the product system to carry out the defined functional unit. Although the different life cycle stages or processes cause emissions of varying amounts of pollutants at specific times throughout the entire life cycle, the result of the inventory phase is an aggregated value for each elementary flow (Owens 1997). This leads to a first bias in life cycle impact assessment (LCIA) since a major emission does not have the same impact

Responsible editor: Mark Huijbregts

**Electronic supplementary material** The online version of this article (doi:10.1007/s11367-014-0779-1) contains supplementary material, which is available to authorized users.

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as a smaller, repeated one. Time boundaries are especially discussed when dealing with long-lived products that involve long-term emissions. For instance, landfill emissions (Pettersen and Hertwich 2008) extend over a long period of time after the end of the operational stage. For this reason, some LCA software and databases differentiate between the short- and long-term emissions (Weidema et al. 2013). However, the choice of specific time boundaries remains open to discussion (Zamagni et al. 2008).

The LCIA characterization phase is also problematic when time is not considered in environmental models (Reap et al. 2008). Since the inventory is aggregated, only continuous loading and simultaneous emissions effects can be taken into account. Fate models of chemicals in the environment are solved at steady state (Reap et al. 2008). Consequently, impacts on the area of protection can only be regarded as an average (Owens 1997).

Moreover, characterization factor calculations are based on the integration of impacts during a given time period. The choice of the integration time frame depends on the stakeholder's perspective and may actually vary from one impact category to another (De Schryver et al. 2011). Many arguments have been put forward to support the use of finite or infinite time horizons or suggest discounting methods to weight impacts over time, but there has yet to be a consensus (Udo de Haes et al. 1999; Hellweg et al. 2003). Changing the time horizon significantly modifies the characterization factors as is the case for climate change (Forster et al. 2007).

The ecotoxicity impact category is particularly sensitive to time since dynamic processes drive the fate of contaminants. Traditionally in LCA, the mass of a pollutant released in the environment (i.e., the inventory result) is proportionally linked to its corresponding impact by a constant characterization factor, but time-dependent processes such as mass transfer phenomena and chemical reactions are responsible for transitory states and induce the nonlinear distribution of the impact over time (Reap et al. 2008).

Ecotoxic impacts are integrated over an infinite time horizon so that long-lived pollutants that theoretically never disappear from the environment, such as metals, have very high characterization factors (Rosenbaum et al. 2008). In recent years, the need to improve metals characterization has been better defined (Diamond et al. 2010). Existing models developed for organic contaminants and requiring chemical properties including half-life time and partition coefficients are not suitable to describe inorganic contaminants. Recently, following recommendations set out as part of an expert workshop (Diamond et al. 2010), research was carried out to include complex mechanisms such as speciation, bioavailability, and particle dissolution (Gandhi et al. 2010; Farley et al. 2011). It was also shown earlier that characterization factors significantly depend on the time horizon selected for integration and on the residence time in the different environmental compartments (Huijbregts et al. 2001).

The integration of impacts over an infinite time horizon as a single result for freshwater ecotoxicity of metals may need to be reconsidered. It may be relevant for decision makers to know how impacts are spread over different time scales. Short-term impacts are likely to be overestimated when using traditional CF values. Nondynamic values are only compatible with quasi-infinite time horizons when adopting a conservative approach. In the case of persistent contaminants such as metals, the dynamic approach questions the ability of common multimedia models to predict fate over such long time frames. Indeed, important uncertainties are associated to the modeling of environmental impacts over several centuries and millennia. For instance, the Intergovernmental Panel on Climate Change (IPCC) has decided in its last assessment report not to provide anymore global warming potential (GWP) values for time horizon of more than 100 years (IPCC 2013).

A dynamic LCA framework has recently been proposed to take into account the timing of emissions in LCA (Levasseur et al. 2010). The dynamic LCA approach consists in developing a temporally disaggregated inventory and then assessing its impact over time using time-horizon-dependent characterization factors. The result is a curve showing the evolution of the potential impact caused by the life cycle emissions over time. Time-horizon-dependent characterization factors have first been developed for global warming, and the method has been applied to a few case studies such as the comparison of bio- and fossil-based fuels including land use change emissions (Levasseur et al. 2010), the assessment of a carbon mitigation project through forestry (Levasseur et al. 2012a), and the consideration of biogenic carbon and temporary storage in LCA (Levasseur et al. 2013). These studies have shown that it is important to consider the timing of emissions to be consistent when assessing global warming impacts over a finite time horizon and that knowing the temporal distribution of these impacts may influence decision making. Recent research projects intend at facilitating the implementation of the dynamic LCA approach in LCA software proposing a method to facilitate the calculation of temporally disaggregated inventories (Beloin-Saint-Pierre et al. 2014) or analyzing the relevance of including temporal information in life cycle inventory databases such as the relative timing of the different processes of a supply chain for instance (Pinsonnault et al. 2014).

In this paper, the dynamic LCA framework, initially developed for the climate change impact category, is extended to address the case of freshwater ecotoxicity impacts of metals. Indeed, the single use of an infinite time horizon may be questioned, and it may be useful for decision makers to look at other time horizons. In this case, it could be important to consider the timing of metals emissions to be consistent in

time frames when assessing impacts. First, time-horizon-dependent characterization factors are developed for freshwater ecotoxicity of metals using the instantaneous contaminant loading in all environmental media following an initial pulse emission. The time-dependent fate of 18 metals for emissions to air, freshwater, sea, and soil was evaluated based on the USEtox multimedia model. Then, the dynamic LCA approach is applied to a case study of zinc fertilization in agriculture to calculate the time-dependent impact of zinc on freshwater ecotoxicity of a temporally disaggregated life cycle inventory. Fertilization was deemed relevant since it involves a product system with emissions occurring over a relatively long time period. The fact that zinc is spread directly on agricultural soil makes it a major contributor to the freshwater ecotoxicity impact category. Finally, conclusions are drawn regarding the influence of the timing of emissions on the assessment of freshwater ecotoxicity of metals in LCA.

## 2 Methods

### 2.1 Development of time-horizon-dependent characterization factors

#### *2.1.1 Description of the multimedia fate model and selection of time-dependent parameters*

The USEtox multimedia model was chosen to calculate the fate of metals in the environment since it is based on a scientific consensus developed under the UNEP-SETAC life cycle initiative (Hauschild et al. 2008; Rosenbaum et al. 2008). The 18 metals studied are Ag(I), As(III), As(V), Ba(II), Be(II), Cd(II), Co(II), Cr(III), Cr(VI), Cu(II), Hg(II), Mo(VI), Ni(II), Pb(II), Sb(III), Sb(V), Se(IV), Sn(II), Tl(I), V(V), and Zn(II). USEtox is a nested multimedia fate model consisting of five compartments (air, freshwater, sea, natural soil, and agricultural soil) at two geographical scales (continental and global scales) with an additional compartment for urban air.

Both removal and intermedia transport processes are included in the model. Fate calculations in USEtox already include time-related data such as intermittent rain and residence times, which are inherent to the environment, and chemical-specific half-lives to account for degradation. Even if metals never degrade (half-lives are set to very high values), sinks enable them to leave the system (marine sediment burial, stratospheric escape, leaching, etc.), thus avoiding infinite characterization factors. Particular partition coefficients between solids, water, organic complexes, and particles are specified in USEtox to describe metal properties and assess the dissolved fraction of substance in freshwater.

In USEtox, the characterization factors (CFs) for ecotoxicity are expressed according to the common equation:

$$CF = FF \times XF \times EF \quad (1)$$

where FF is the fate factor (day), XF is the exposure factor ($kg_{dissolved}\ kg^{-1}$), and EF is the effect factor (PAF $m^3$ $kg^{-1}{}_{dissolved}$). CF (PAF $m^3$ day $kg^{-1}$) represents the potentially affected fraction of species due to a pulse emission of 1 kg over an infinite time horizon.

The fate factor FF is assumed to be the only time-dependent parameter to consider for the development of time-horizon-dependent CFs. Exposure XF and effect factors EF are presumed constant so that the effect of the contaminant on ecosystems remains the same over time. In fact, the exposure factor XF may also be sensitive to time. It expresses that the fraction of metal dissolved and dissolution processes are also time-dependent since they are not always instantaneous. However, it is considered outside the scope of this paper and could be addressed in a future research project to develop improved time-horizon-dependent CFs.

#### *2.1.2 Calculation of time-horizon-dependent fate factors from USEtox*

A system of differential equations providing the mass variation of a given metal in each environmental compartment through time $\frac{\overrightarrow{dM}}{\overrightarrow{dt}}$ (kg $day^{-1}$) is set using the matrix algebra framework (Rosenbaum et al. 2007).

$$\frac{\overrightarrow{dM}}{\overrightarrow{dt}} = \overrightarrow{k}\overrightarrow{M} + \overrightarrow{S} \quad (2)$$

Where $\overrightarrow{k}$ is the matrix of rate constants in each compartment taken from USEtox ($day^{-1}$), $\overrightarrow{M}$ is the vector of resulting mass of metal in the respective environmental compartments (kg), and $\overrightarrow{S}$ is the vector of continuous emission fluxes in each compartment (kg $day^{-1}$). The matrix $\overrightarrow{k}$ is chemical-specific and describes the first-order intermedia transfer and degradation processes occurring in each environmental compartment.

Multimedia fate models, as defined by Mackay and Seth (1999), are traditionally solved at steady-state conditions $\frac{\overrightarrow{dM}}{\overrightarrow{dt}} = 0$, assuming continuous fluxes (kg $day^{-1}$) as shown here. While this is a common situation for risk assessment, in LCA, one needs to characterize a pulse emission (kg). Multimedia fate models were still proven valid for LCA, as it was demonstrated that the cumulative mass load of a pulse emission over an infinite time equals the steady state mass

load of an equivalent continuous emission (Heijungs 1995; Pennington et al. 2006).

We propose to solve Eq. (2) numerically using a time integration software (e.g., MATLAB or Python) which provides the dynamics of the mass of contaminant $M(t)$ (kg) in each compartment. Instead of using continuous emission fluxes, the system of equations is solved for an initial condition of a unit mass pulse emission occurring in a given compartment. FF($t$) (kg day kg$^{-1}_{\text{released}}$) is then obtained for different compartments of emission using Eq. (3) by integrating $M(t)$ from 0 to $t$.

$$\mathrm{FF}(t) = \int_0^t M(t)dt \tag{3}$$

### 2.1.3 Time-horizon-dependent CFs

Cumulative CFs $\mathrm{CF_c}(t)$ (PAF m$^3$ day kg$^{-1}$) express the potential integrated impact from $t$=0 (time of pulse emission) to $t$ and are derived using Eq. (4). Cumulative CFs at the infinity are expected to converge toward traditional CFs calculated with the steady-state USEtox model.

$$\mathrm{CF_c}(t) = \mathrm{FF}(t) \times \mathrm{XF} \times \mathrm{EF} \tag{4}$$

Instantaneous CFs $\mathrm{CF_i}(t)$ (PAF m$^3$ day kg$^{-1}$) represent the potential impact generated at a given year $t$ following a pulse emission at year $t$=0. They are derived using Eq. (5).

$$\mathrm{CF_i}(t) = [\mathrm{FF}(t) - \mathrm{FF}(t-1)] \times \mathrm{XF} \times \mathrm{EF} \tag{5}$$

## 2.2 Application to a case study on zinc fertilization

### 2.2.1 Product system, functional unit, and inventory data

Some metals qualified as essential elements are necessary for living organisms. The Food and Agriculture Organization (FAO) of the United Nations recently identified zinc as the most deficient micronutrient in agricultural soil (International Zinc Association 2010). Lack of zinc in soil leads to a decrease in crop yields and affects human health since zinc concentrations in grains are not sufficient to supply zinc through food. Zinc fertilizers are touted as promising solutions to soil deficiency. Different forms of zinc, such as zinc sulfate, zinc oxide, and zinc-EDTA chelate, are usually spread on crops. The functional unit used for this case study is the fertilization required according to best practices to produce 1 t per year of corn for 20 years (9 kg ha$^{-1}$ every 3 years). Zinc oxides are used for fertilization.

The studied product system goes from zinc oxide secondary production to fertilizer spreading, as represented in Fig. 1.

The three processes are supposed to take place in the same year for each fertilizer application. Material technology corporation Umicore provided the annual data for the production of technical oxide and zinc oxide in 2010.

Soils are assumed to be zinc deficient, and a common application rate of 9 kg ha$^{-1}$ every 3 years is used (Alloway 2004). Zinc deficiency and transfer to plant depend on many parameters, including soil properties (pH, alkalinity, etc.) and local agricultural management. Despite the variability of the data used in this work, impact interpretations are consistent since the aim is to compare dynamic and nondynamic results.

Transportation between locations is assessed using the ecoinvent processes transport, lorry >28 t, fleet average/CH U for road and transport, transoceanic tanker/OCE U for sea. Umicore provided raw materials transport distances, and an average distance between locations is used to estimate other transportation steps related to final product distribution (6,300 km by sea and 1,200 km by road; Illinois, USA, delivery location was used as reference).

Inventory data for one spreading is presented in Table 1. The same mass loadings are then repeated every 3 years. Zinc emissions take several forms: ion, oxides, chloride, and zinc. Three compartments are involved: air, water, and soil. In the current context, the corresponding USEtox compartments are allocated to urban air, continental freshwater, and agricultural soil.

The emissions of metallic zinc, zinc ion, and zinc chloride are assumed to be immediately available. This assumption is a coarse simplification since metallic zinc takes time to dissolve, delaying the impact of such an emission. However, the amount of metallic zinc released to the environment is low compared the other emissions (see Table 1) so that its dissolution kinetics would probably not affect significantly the results. Zinc oxide is a sparingly soluble compound and therefore may require some time to dissolve. Moreover, once dissolved, zinc is submitted to speciation equilibriums that are not considered in this publication. Spreading application frequency appears to be highly variable, and a sensitivity analysis is performed. The results are calculated for three spreading rates: 3 kg ha$^{-1}$ every year, 9 kg ha$^{-1}$ every 3 years and 18 kg ha$^{-1}$ every 6 years. The amount of fertilizer spread is adjusted so that the total amount of zinc applied over the 20-year period remained the same in each case. Rate variation intervals seem realistic, as verified in the literature (Alloway 2004).

Zinc oxide dissolution kinetics is scarcely detailed in the literature and depends on particle size (European Commission 2004). Since the influence of dissolution is expected to be significant, two series of calculations are conducted. The first ignores zinc oxide dissolution (as if it were instantaneous), and the second accounts

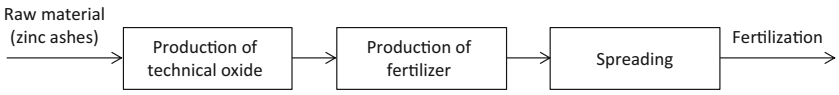


**Fig. 1** System boundaries for the case study of zinc fertilization

for it. To account for dissolution, a succession of small pulse emissions over time is considered instead of a single pulse emission and added to the disaggregated inventory. A first-order kinetic model is used to calculate the dissolution emissions following data provided by Umicore. The rate constant $a$ (0.041 $day^{-1}$) is based on dissolution tests conducted under the European Union risk assessment program (European Commission 2004). These tests were performed in water under standardized conditions, but no data for dissolution in water contained in soils are available. Since dissolution in soils may be slower, a sensitivity analysis is performed using a rate constant half as high (0.0205 $day^{-1}$). Equation (6) is used to calculate the amount of metal $M$ (kg) that is dissolved on day $t$ following a pulse emission of $M_0$ (kg). The objective of this second calculation is to analyze the importance of dissolution kinetics on the temporal distribution of impacts.

$$\mathrm{M}(t) = M_0\left[\mathrm{e}^{-\mathrm{at}} - \mathrm{e}^{-\mathrm{a}(t\,-\,1)}\right] \tag{6}$$

*2.2.2 Impact assessment calculations*

Freshwater ecotoxicity impacts are calculated using the dynamic LCA framework (Levasseur et al. 2010) by coupling the temporally disaggregated inventory with time-horizon-dependent CFs. Calculations are carried out using instantaneous and cumulative CFs. Emissions to urban air, continental freshwater, and agricultural soil are treated separately with their corresponding CFs and then added. Hence, impacts at time $t$ sum all the impacts generated by the emissions $E$ (kg) taking place between time 0 and time $t$: Emission at time $t$ is multiplied by CF at time 0, emission at time $t-1$ is multiplied by CF at time 1, and so on. Eventually, emission at time 0 is multiplied by CF at time $t$. Thus, the total cumulative and instantaneous impacts $I_c(t)$ (PAF $m^3$ day) and $I_i(t)$ (PAF $m^3$ day) are calculated using Eqs. (7) and (8).

$$I_c(t) = \sum\nolimits_{k\,=\,0}^{t} \mathrm{E(k)} \times \mathrm{CF_c}(t-\mathrm{k}) \tag{7}$$

$$I_i(t) = \sum\nolimits_{k\,=\,0}^{t} \mathrm{E(k)} \times \mathrm{CF_i}(t-\mathrm{k}) \tag{8}$$

## 3 Results and discussion

### 3.1 Characterization factors

As an illustration, the instantaneous and cumulative CFs for a pulse emission of zinc in freshwater, urban air, and soil are presented in Fig. 2. As expected, the cumulative CF at the infinity converges toward the traditional CF calculated with the steady-state USEtox model. Similar figures can be drawn for the 18 metals assessed and the five compartments of emission considered. The results are provided in the Electronic Supplementary Material.

The dynamics of impacts depends on two important parameters: the compartment of emission and the metal type. The compartment of emission significantly influences the shape of the curve since it determines the convergence speed of the cumulative CF. For a freshwater emission, the metal is in direct contact with the aquatic ecosystem, and the impacts therefore take place immediately. The maximum amount of metal reaching the compartment corresponds to the mass released. The extent of the impacts on freshwater ecosystems thus depends on each metal's ability to leave the freshwater compartment, which is usually very fast unless the freshwater reservoir is very large and implies a long residence time.

With regards to the indirect emissions such as emissions to air and soil (urban air, continental air, agricultural soil, and natural soil in USEtox), the maximum amount of metal reaching freshwater is lower. Metals are submitted to diffusive

**Table 1** Inventory data corresponding to one spreading for spreadings occurring every 3 years

| Processes | Mass (kg) and form of emission | | |
|---|---|---|---|
| | Air | Water | Soil |
| Transportation of raw materials | Zn $3.94.10^{-11}$ | Zn ion $1.87.10^{-11}$ | Zn $7.72.10^{-13}$ |
| Production of technical oxide | $ZnCl_2$ $1.43.10^{-9}$ | | |
| Transportation of technical oxide | Zn $1.44.10^{-11}$ | Zn ion $7.39.10^{-13}$ | Zn $4.42.10^{-14}$ |
| Production of fertilizer | ZnO $2.6010^{-08}$ | Zn $1.23.10^{-08}$ | |
| Transportation of fertilizer | Zn $1.41.10^{-09}$ | Zn ion $1.07.10^{-09}$ | Zn $1.03.10^{-11}$ |
| Spreading | | | ZnO $1.26.10^{-3}$ |

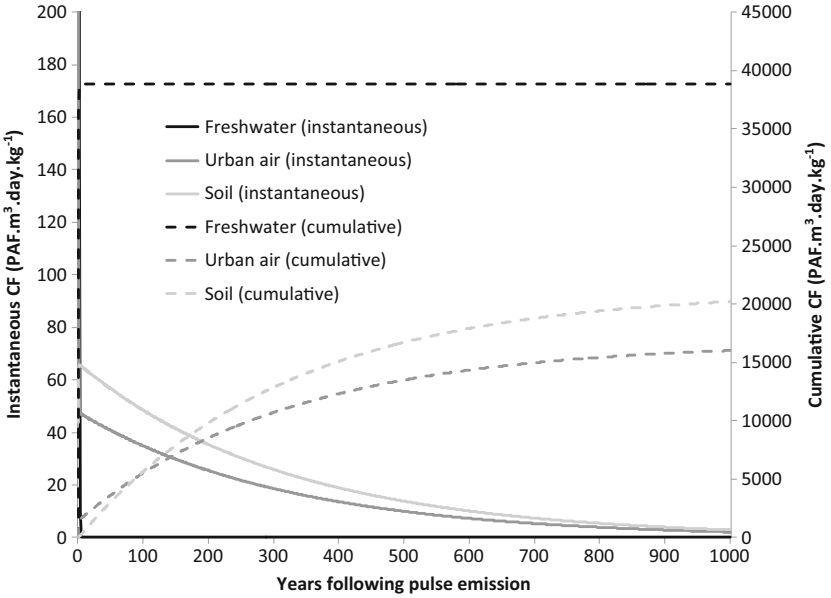


**Fig. 2** Instantaneous and cumulative time-horizon-dependent CFs for an emission of zinc to freshwater, urban air, and soil compartments. An emission to freshwater reaches its total impact value much faster than emission to urban air or to soil. Cumulative CFs would reach the USEtox value for an infinite time horizon

and convective transport mechanisms that disperse contaminants between several intermediary compartments. Moreover, the time required to pass through freshwater is correlated with the characteristic times of input intermedia transfers. Considering that metals are not volatile, transfer from air to water is fast. In contrast, metal runoff from soil is a slow process that occurs over a long period of time since soil retains contaminants, limiting transfers to freshwater. The cumulative CF at infinity is thus higher for an emission to soil but is increasing more slowly than the cumulative CF of an emission to urban air.

The behavior of CFs over time also differs for each metal. CFs for zinc are compared to those of nickel and mercury for an emission to urban air in Fig. 3.

The persistence time and the maximum mass of metal reaching the freshwater compartment depend on the type of metal. An analysis of the matrix of mass balance rate constants for metals in USEtox reveals that removal processes (from freshwater and seawater) and intermedia transfers between soil (agricultural and natural) and water are chiefly responsible for the variation since they are the parameters that differ the most from one metal to another. These processes depend on landscape properties and chemical-specific properties such as partition coefficients in freshwater between water and particle (Kd suspended solid/freshwater) and partition coefficients between organic complexes and water (Kd soil particles/water).

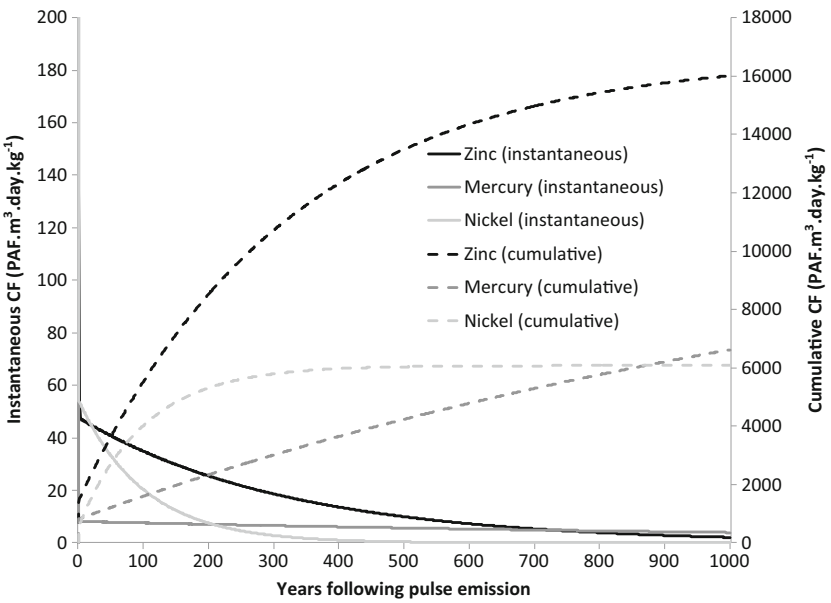


**Fig. 3** Instantaneous and cumulative time-horizon-dependent CFs of Zn, Ni, and Hg for an emission to urban air. The type of metal influences the total impact value, but also the rate at which this value is reached

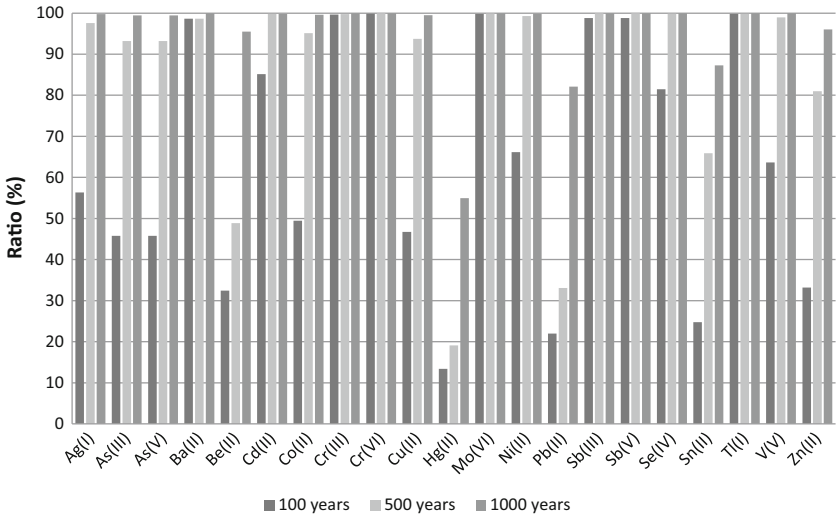


**Fig. 4** Ratio of the cumulative CF calculated for a given time horizon (100, 500, and 1,000 years) and the cumulative CF calculated for an infinite time horizon for 18 metals

These coefficients control the quantity of the metal linked to the solid particle, explaining why certain metals tend to be adsorbed on soil particles or sediments. Indeed, partition coefficients of mercury are orders of magnitude higher than those of nickel: Kd (suspended solid/freshwater)=$2.10^4$ L $kg^{-1}$ and Kd (soil particles/water)=$7.52.10^5$ L $kg^{-1}$ for Ni as compared to Kd (suspended solid/freshwater)=$2.5.10^5$ L $kg^{-1}$ and Kd (soil particles/water)=$1.57.10^6$ L $kg^{-1}$for Hg. The adsorption of metals on solid particles increases their accumulation in soils, which is an intermediary compartment that can act as a temporary reservoir so that Hg has a higher residence time in the soil compartment than Ni. Ni thus ends up in freshwater more quickly than Hg. As a consequence, even if Hg escapes more quickly from freshwater than Ni—due to its higher affinity with sediments—the influence of intermediary compartments limits the impact of Ni to a shorter time frame than Hg.

The results obtained in this study are only valid for the landscape and chemical parameters modeled in USEtox, and the results obtained for the dynamic resolution of another multimedia model could be different. A lot of uncertainty is related to these parameters in multimedia models, and some of them, such as speciation and bioavailability, are not considered in this paper. The inclusion of these parameters may add to the complexity of developing improved time-horizon-dependent CFs.

It is confirmed that cumulative CFs converge toward traditional CF values for each metal, thus validating that no mistakes have been made while solving the mass balance equations dynamically. In the case of indirect emissions (in compartments other than freshwater), CFs may only converge after thousands of years. In the case of a direct emission to freshwater, cumulative CFs reach their final value within 1 year. These time spans are consistent with previous observations for different compartments of emission by Guinée et al. (1999),

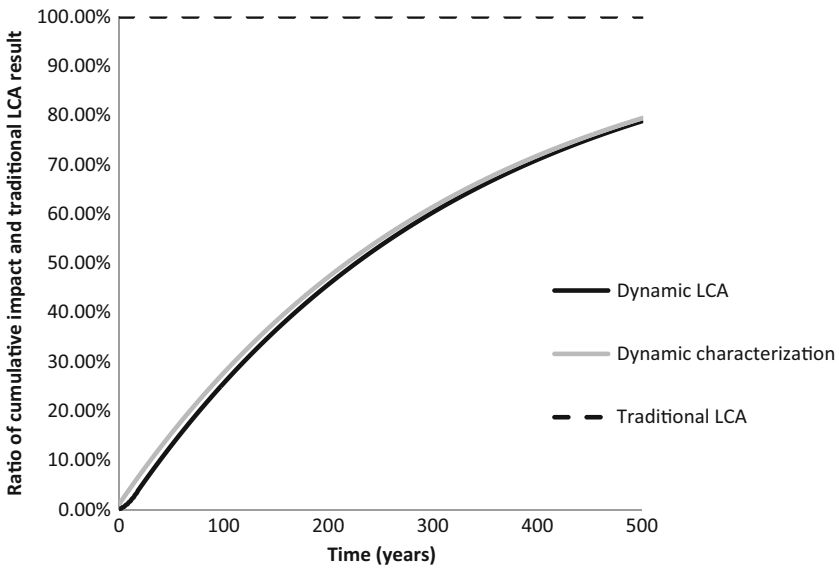


**Fig. 5** Ratio of the cumulative impact calculated with two dynamic approaches and the impact calculated with a traditional LCA approach for the case study of zinc fertilization ((1) dynamic LCA for which time-horizon-dependent CFs are used to assess a disaggregated inventory and (2) dynamic characterization for which time-horizon-dependent CFs are used to assess an aggregated inventory)

**Table 2** Ratio of the cumulative impact calculated with dynamic LCA and the impact calculated with traditional LCA for the case study of zinc fertilization for four time horizons (20, 100, 500, and 1,400 years)

| Time horizon (years) | 20 | 100 | 500 | 1,400 |
|---|---|---|---|---|
| Impact (% of total value) | 4 | 25 | 79 | 99.9 |

who reported minimum times between 200 years for a cadmium emission to soil and 80,000 years for a lead emission to soil to reach steady state. Work of Guinée et al. also confirmed fate variations between direct and indirect emissions.

As shown in Fig. 4, the time horizon chosen for impact assessment is also a critical parameter.

For nickel and zinc, the cumulative CF values after 100 years are respectively two and three times lower than the cumulative CF value for an infinite time horizon. Differences induced by the choice of a time horizon are observed for most of the USEtox metals. Nine metals do not reach 50 % of their final impact within 100 years, and three (Be, Hg, and Pb) take more than 500 years. Such CF variations based on the time horizon support the results obtained by Huijbregts et al. (2001), which evoke differences of several orders of magnitude between CFs calculated for infinite vs. shorter time horizons.

### 3.2 Case study

Figure 5 compares the cumulative impact of zinc fertilization on freshwater ecotoxicity calculated with traditional and dynamic LCA approaches. Three curves are presented: The black curve considers inventory disaggregation and dynamic characterization (the full dynamic LCA approach presented in Section 2), the gray curve shows the dynamic characterization of an aggregated inventory (the time-horizon-dependent CFs are applied to equivalent aggregated pulse emissions occurring at time zero), and the dotted line presents the value obtained with a traditional LCA approach.

Dynamic LCA results are always lower than traditional LCA results. Figure 5 shows minor differences between the results of the dynamic characterization of an aggregated inventory and the full dynamic LCA approach. For this particular case study, the use of time-horizon-dependent CFs is more important in determining the dynamics of impacts than the timing of emissions. Zinc fertilization was studied for a 20-year treatment. Thus, the influence of inventory disaggregation on the temporal impact profile is limited to the first 20 years. As shown previously, time-horizon-dependent CFs do not converge before hundreds of years, and the impact of dynamic characterization dominates over inventory disaggregation, especially for short time horizons. The results for aggregated emissions are higher for any finite time horizon since the pollutants are considered released earlier.

Table 2 presents the ratio between the dynamic and traditional LCA results for four time horizons. The traditional LCA result consists in multiplying the aggregated inventory with the corresponding CFs obtained with the USEtox steady-state model.

Only 4 % of the total impact actually takes place during the life cycle time frame (20 years). For a 100-year time horizon, the impact is divided by four as compared to a nondynamic approach. Finally, for a 500-year time horizon, the calculated impact is 21 % less. The result obtained with the dynamic LCA approach converges toward the traditional LCA result for a time horizon of over 1,400 years.

More than 99 % of the impact is due to the use phase of the fertilizer, and the spreading application frequency therefore appears to be a determining parameter. As a result, a sensitivity analysis is carried out. Figure 6 shows that the impact depends on the spreading application

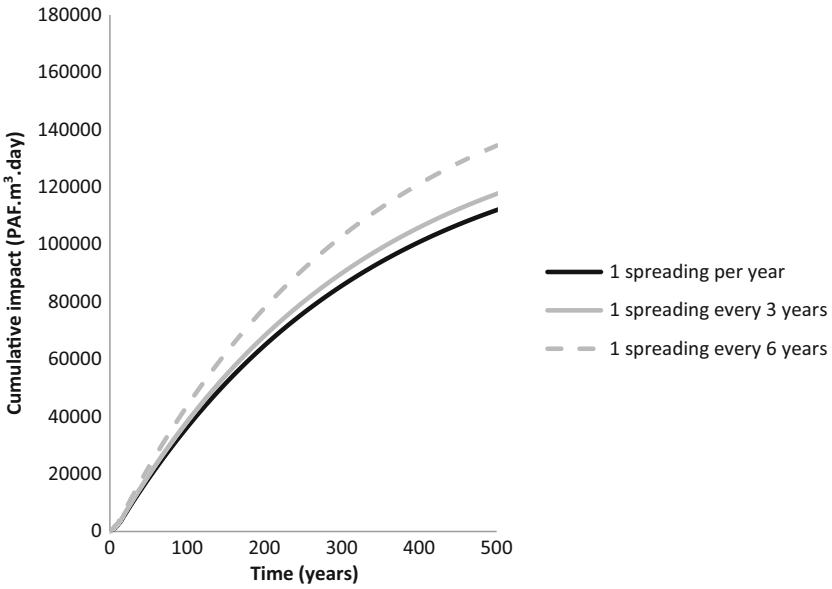


**Fig. 6** Result of the cumulative impact at different time horizons for the case study of zinc fertilization for different spreading application frequencies

frequency. Rate modification changes the profile of the results over many years. Once again, the more aggregated the emissions, the greater the impacts. Users should take note of this sensitive parameter.

The kinetics of zinc oxide dissolution does not affect the results for this case study since almost everything is dissolved during the first year, which is relatively restricted as compared to the duration of the impact. For the initial rate constant considered (0.041 $day^{-1}$), the cumulative impact 1 year after a given emission is 91 % of the cumulative impact calculated considering instantaneous dissolution, and it is 85 % for a rate constant half as high (0.0205 $day^{-1}$). The cumulative impact is the same 10 years after the emission for instantaneous dissolution and for both dissolution rate constants. Considering that zinc oxide dissolves almost instantaneously, the assumption is acceptable. But, this is not necessarily the case for all particles, and it depends on the characteristic time of the first decay kinetic. In this case, the characteristic time was less than 365 days, which corresponds to the calculation time step. However, the influence of dissolution could be significant with characteristic times greater than 1 year that are of the same order of magnitude than the time frame of the study. The kinetics of dissolution could eventually be integrated in XF to improve CFs.

## 4 Conclusions

The dynamic approach provides relevant information on the intensity, extent, and frequency of the impacts for the freshwater ecotoxicity of metals. Dynamic processes depend on the nature of the metals and the compartments of emission. Other environmental mechanisms such as speciation could also have a significant impact on fate and will be studied in the future. Indeed, bioavailability and metal forms of emission (that follow specific particulate dissolution processes) are responsible for metal toxicity (Diamond et al. 2010). An approach was proposed to consider bioavailability in traditional CFs in LCA (Gandhi et al. 2010). Future research to include this approach in time-horizon-dependent CFs could improve their accuracy.

The case study of zinc fertilization shows that the use of time-horizon-dependent CFs enables assessing freshwater ecotoxicity impacts of metals over time, allowing decision makers to test the sensitivity of their results to the choice of a time horizon. The question of time preferences is often discussed when dealing with time horizons for impact assessment or with discounting of emissions (Hellweg et al. 2003). The integration of impacts over an infinite time horizon ensures that impacts are not pushed back in the future harming future generations. However, the uncertainty of the models when used over such long time frames and the absence of consideration for future potential mitigation actions are arguments to look at shorter time horizons (Levasseur et al. 2012b). Thus, it may be relevant for decision makers to know how impacts are over different time scales, especially when dealing with freshwater ecotoxicity of metals since impact occurs over several centuries.

It has been shown for global warming that the use of CFs integrated over finite time horizons may lead to inconsistencies in time frames when assessing inventories over long time periods (Levasseur et al. 2010). The same conclusion can be drawn for freshwater ecotoxicity impacts if time-horizon-dependent CFs are used to assess metal emissions occurring over a long period of time. Coupling a temporally disaggregated inventory with time-horizon-dependent CFs using the dynamic LCA approach is likely to become essential in order to consistently reconcile the time boundary of the system and the time horizon used for impact assessment. This will be valuable especially when studying systems with long operational times such as infrastructures, agriculture processes, or end-of-life management. For systems with short operational times, the use of time-horizon-dependent CFs with an aggregated inventory may be sufficient.

**Acknowledgments** The authors would like to thank Umicore for its inputs to the project. The International Life Cycle Chair (a research unit of the CIRAIG) would like to acknowledge the financial support of its industrial partners: Arcelor Mittal, Bombardier, Hydro-Québec, LVMH, Michelin, Mouvement des caisses Desjardins, Nestlé, RECYC-QUÉBEC, RONA, SAQ, Solvay, Total, Umicore, and Veolia Environnement.

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